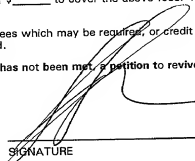


| | | |
|--|---|--|
| FORM-PTO-1390 (Rev. 12-29-99) | U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE | ATTORNEY'S DOCKET NUMBER |
| TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371 | | 022701-912 U.S. APPLICATION NO. (if known, see 37 C.F.R. 1.5) 09/720362 |
| INTERNATIONAL APPLICATION NO. PCT/FR99/01378 | INTERNATIONAL FILING DATE 10 June 1999 | PRIORITY DATE CLAIMED 22 June 1998 |
| TITLE OF INVENTION METHOD FOR TREATING BY COMBUSTION CARBON-CONTAINING PARTICLES IN AN INTERNAL COMBUSTION ENGINE EXHAUST CIRCUIT | | |
| APPLICANT(S) FOR DO/EO/US Gilbert BLANCHARD; William MUSTEL; Thierry SEGUELONG | | |
| Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information: | | |
| 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. | | |
| 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. | | |
| 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and the PCT Articles 22 and 39(1). | | |
| 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. | | |
| 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) | | |
| a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). | | |
| b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau. | | |
| c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US) | | |
| 6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). | | |
| 7. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) | | |
| a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). | | |
| b. <input type="checkbox"/> have been transmitted by the International Bureau. | | |
| c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. | | |
| d. <input type="checkbox"/> have not been made and will not be made. | | |
| 8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). | | |
| 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). | | |
| 10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). | | |
| Items 11. to 16. below concern other document(s) or information included: | | |
| 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. | | |
| 12. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. | | |
| 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. | | |
| <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. | | |
| 14. <input type="checkbox"/> A substitute specification. | | |
| 15. <input type="checkbox"/> A change of power of attorney and/or address letter. | | |
| 16. <input type="checkbox"/> Other items or information: | | |

| | | | | | |
|--|--------------|-------------------------------|------------------|---|-------|
| U.S. APPLICATION NO. (If known, enter 37 CFR 1.101) | | INTERNATIONAL APPLICATION NO. | | ATTORNEY'S DOCKET NUMBER | |
| 097720362 | | PCT/FR99/01378 | | 022701-912 | |
| 17. <input checked="" type="checkbox"/> The following fees are submitted: | | | | CALCULATIONS | |
| Basic National Fee (37 CFR 1.492(a)(1)-(5)): Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1,000.00 (960) International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$860.00 (970) International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$710.00 (958) International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$690.00 (956) International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 (962) | | | | | |
| ENTER APPROPRIATE BASIC FEE AMOUNT = | | | | \$ 860.00 | |
| Surcharge of \$130.00 (154) for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)). | | | | 20 <input type="checkbox"/> 30 <input type="checkbox"/> | |
| Claims | Number Filed | Number Extra | Rate | | |
| Total Claims | 25 -20 = | 5 | X\$18.00 (966) | \$ | 90.00 |
| Independent Claims | 1 -3 = | 0 | X\$80.00 (964) | \$ | -- |
| Multiple dependent claim(s) (if applicable) | | | + \$270.00 (968) | \$ | |
| TOTAL OF ABOVE CALCULATIONS = | | | | \$ 950.00 | |
| Reduction for 1/2 for filing by small entity, if applicable. Verified Small Entity statement must also be filed. (Note 37 CFR 1.9, 1.27, 1.28). | | | | | |
| SUBTOTAL = | | | | \$ 950.00 | |
| Processing fee of \$130.00 (156) for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492(f)). | | | | 20 <input type="checkbox"/> 30 <input type="checkbox"/> | |
| TOTAL NATIONAL FEE = | | | | \$ 950.00 | |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 (581) per property + | | | | | |
| TOTAL FEES ENCLOSED = | | | | \$ 950.00 | |
| | | | | Amount to be: | |
| | | | | refunded \$ | |
| | | | | charged \$ | |
| a. <input type="checkbox"/> A check in the amount of \$ 950.00 to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. 02-4800 in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 02-4800. A duplicate copy of this sheet is enclosed. | | | | | |
| NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status. | | | | | |
| SEND ALL CORRESPONDENCE TO: | | | | | |
| Norman H. Stepno BURNS, DOANE, SWECKER & MATHIS, L.L.P. P.O. Box 1404 Alexandria, Virginia 22313-1404 (703) 836-6620 | | | | | |
| SIGNATURE  Teresa Stanek Rea NAME 30,427 REGISTRATION NUMBER | | | | | |

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of)
Gilbert BLANCHARD et al.)
Application No.: Unassigned) Group Art Unit: Unassigned
(Corresponds to PCT/FR99/01378))
International Filing Date: 10 June 1999) Examiner: Unassigned
For: METHOD FOR TREATING BY)
COMBUSTION CARBON-)
CONTAINING PARTICLES IN AN)
INTERNAL COMBUSTION ENGINE)
EXHAUST CIRCUIT)
)

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Prior to examination, please amend the above-captioned application as follows:

IN THE CLAIMS:

Kindly amend the claims as follows:

1. (Amended) Process for the combustion treatment of carbonaceous particles collected on a filter situated in an exhaust circuit of an internal combustion engine, [characterized in that the combustion of the] comprising contacting said particles [is brought about by contacting them] with a gas mixture comprising at least nitrogen dioxide generated within the exhaust circuit of [the] said engine, [the] and thus combusting same, said

particles having been seeded prior to their combustion thereof with at least one oxidation
catalyst [of their oxidation] therefor.

Claim 2, line 1, change "characterized in that" to --wherein--;
line 2, delete "the" and after "metals" (second occurrence) insert

--,--;

line 3, delete "and" (first occurrence) and delete "such as manganese,
iron, copper, sodium, nickel and scandium,".

Claim 3, line 1, change "either of claims 1 and 2" to --claim 1-- and change
"characterized in that" to --wherein--;

line 2, delete "the".

Claim 4, line 1, change "characterized in that" to --wherein--;
line 2, after "from" insert --the group consisting of--.

Claim 5, line 1, delete "or 4" and change "characterized in that" to
--wherein--;

line 2, change "containing" to --comprising--;

line 3, delete ", such as";

line 4, delete in its entirety;

line 5, delete "and iron".

Claim 6, line 1, change "one of claims 2 to 5" to --claim 2--; and change "characterized in that" to --wherein--.

Claim 7, line 1, change "one of claims 1 to 6" to --claim 1-- and change "characterized in that" to --wherein--;
line 3, delete "such as a salt, sol or organic complex".

Claim 8, line 1, change "one of claims 1 to 6" to --claim 1-- and change "characterized in that" to --wherein--.

Claim 9, line 1, change "one of claims 1 to 8" to --claim 1-- and change "characterized in that" to --wherein--;
line 3, delete "preferably between 0.1% and 15%,".

Claim 10, line 1, change "characterized in that" to --wherein--;
line 2, delete "and, preferably, at least 2%".

Claim 11, line 1, change "one of claims 1 to 10" to --claim 1-- and change "characterized in that" to --wherein--;
line 2, delete "the" (second occurrence).

Claim 12, line 1, change "one of claims 1 to 10" to --claim 1-- and change "characterized in that" to --wherein--;

line 2, delete "the" (second occurrence).

Claim 13, line 1, change "one of claims 1 to 10 and 12" to --claim 1-- and change "characterized in that" to --wherein--.

Claim 14, line 1, change "characterized in that" to --wherein--.

Claim 15, line 1, change "characterized in that" to --wherein--.

Claim 16, line 1, delete "or 15" and change "characterized in that" to --wherein--;

line 5, delete "the".

Claim 17, line 1, change "one of claims 1 to 10 and 12 and 13" to --claim 1--;

lines 1-2, change "characterized in that" to --wherein--.

Claim 18, line 1, change "characterized in that" to --wherein--.

Claim 19, line 1, change "characterized in that" to --wherein--.

Claim 20, line 1, change "one of claims 10 and 12 to 19" to --claim 10-- and change "characterized in that" to --wherein--;

lines 3-4, change "such as metal oxides of the platinum group, for instance rhodium oxide, Rh_2O_3 or the like as well as" to --and--;

lines 5-6, delete "such as transition metal oxides such as those based on cerium and/or manganese, such as CeO_2 , Mn_2O_3 , $\text{Mn}_2\text{O}_3\text{-CeO}_2$, $\text{Mn}_2\text{O}_3\text{-CeO}_2\text{-ZrO}_2$ and the perovskite systems".

Claim 21, line 1, change "characterized in that" to --wherein--.

Claim 22, line 1, change "characterized in that" to --wherein--.

Claim 23, line 1, change "one of claims 12 to 22" to --claim 12-- and change "characterized in that" to --wherein--.

line 2, delete "so-called".

Claim 24, line 1, change "characterized in that" to --wherein--.

line 4, after "from", add "the group consisting of--.

line 6, after "from" add --the group consisting of--.

Claim 25, line 1, change "one of claims 1 to 10 and 12 to 22" to --claim 1-- and change "characterized in that" to --wherein--;

line 6, delete "the" (third occurrence).

REMARKS

Entry of the foregoing amendments are respectfully requested.

Should the Examiner have any questions concerning the subject application, a telephone call to the undersigned would be appreciated.

Respectfully submitted,

BURNS, DOANE, SWECKER & MATHIS, L.L.P.

By: 

Teresa Stanek Rea
Registration No. 30,427

P.O. Box 1404
Alexandria, Virginia 22313-1404
(703) 836-6620

Date: December 22, 2000

The present invention relates to a process for reducing the harmful emissions of internal combustion engines and significantly limiting their carbonaceous discharges.

5 It relates more particularly to the conjoint use of at least one oxidation catalyst for the said carbonaceous particles and of nitrogen dioxide for the combustion of the carbonaceous matter issuing from internal combustion engines.

10 When fuels are burnt, the carbonaceous products or hydrocarbons form, in their combustion products, carbonaceous particles which are also referred to, in the remainder of the description, by the expression "soot(s)"; which are reputed to be
15 harmful both to the environment and to health. Moreover, these soots deposit on all of the internal walls of the engine and may give rise to malfunctions, especially in turbochargers.

Consequently, the search has long been on for
20 techniques which make it possible to reduce the emission of these carbonaceous particles. This search is, moreover, concomitant with the requirement not to increase the emission of carbon monoxide and of harmful and mutagenic gases such as oxides of nitrogen.

25 A very great number of solutions have been proposed for reducing these carbonaceous emissions.

Among these solutions, the technique employed most widely consists in adapting in the exhaust

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circuits a filter capable of halting all or a very great proportion of the carbonaceous particles produced by the combustion of the various fuels. Filters have therefore been produced which, when installed in the exhaust circuits, allow soot emissions to be reduced by at least 85% by mass.

The problem to be solved then moved to the level of these filters. Accumulating progressively in the filters, the soots cause firstly an increase in pressure loss and, secondly, the beginning of an occlusion which leads to a drop in performance of the internal combustion engine.

The research efforts then shifted to the burning of soots collected by these filters.

This so-called burning operation is extremely delicate in terms of its provision and implementation.

It is possible to bring about the combustion of the soots intermittently either by an electrical heater or by a burner or any other technique employing an external energy source.

Another solution consists in drawing the heat required to ignite these soots from the engine itself, so as to heat the soots accumulated in the filter and in so doing to bring about their inflammation (temperature of the order of 500-600°C).

It has also been proposed to introduce inflammation catalyst precursors into the various fuels

so as to lower the inflammation temperature of the soots.

Another solution is aimed at utilizing oxidation catalysts based on noble metals deposited on supports based on alumina or titanium. They make it possible to facilitate, at low temperature, the oxidation of the carbon monoxide and gaseous hydrocarbons emitted by diesel engines. The discharge of carbon monoxide and hydrocarbons unburnt at 300°C is thereby reduced significantly, to the order of 80 to 90%. However, it is important to note that these catalysts have no oxidizing action whatsoever on the carbonaceous fraction of the soots and, furthermore, have the disadvantage of discharging into the atmosphere not inconsiderable amounts of nitric acid, which give rise to an increase in the acid rains harmful to man and the environment. However, as mentioned before, the search for a solution to the combustion of the soots is concomittant with the requirement not to increase the emission of carbon monoxide nor of gases reputed to be mutagenic and toxic, such as oxides of nitrogen.

One of the most interesting solutions to date consists in adding directly to the fuels an additive deriving from transition metals, alkali metals, alkaline earth metals and/or rare earth metals (EP 0 599 717). The combustion of these soots is

significantly improved by this means. However, for the oxidation of these soots to be optimum, it remains necessary for the temperature of the gases to be treated to be at least of the order of 300°C.

- 5 Another proposed solution takes advantage of the composition of the exhaust gases emerging from diesel engines. Generally, these gases comprise significant amounts of oxides of nitrogen (NO, NO₂), oxygen, carbon monoxide, carbon dioxide, water and, if
- 10 appropriate, sulphur dioxide. Thus the patent EP 341 832 proposes converting this nitrogen monoxide into nitrogen dioxide by catalytic oxidation and using the resultant nitrogen oxide as an oxidizing agent for the particles of carbon accumulated on the filter.
- 15 However, the temperature conditions within which combustion takes place are narrow. They are limited to a temperature of between 250°C and 400°C. Finally, it appears that the reaction rate of oxidation of the carbonaceous particles by nitrogen dioxide is reduced
- 20 not inconsiderably by the sulphur dioxide and when the ratio between the oxides of nitrogen (NO + NO₂) and the carbon formed by the engine is insufficient.

- The object of the present invention is more particularly to provide a novel treatment process which
- 25 makes it possible specifically to optimize the combustion of carbonaceous particles within a significantly widened temperature range.

Unexpectedly, the inventors found, in fact, that when the oxidation of soots by nitrogen dioxide is conducted in the presence of a soot oxidation catalyst, 15 also denoted hereinbelow by the name "SOC", it is possible to effect their combustion within a significantly widened temperature range.

The process claimed also enables the
25 combustion of particles in a wide temperature range,
which corresponds to that encountered for diesel engine
exhaust gases. Therefore, in contrast to other
processes, the process of the invention is effective at

a very low exhaust temperature, i.e. at less than 250°C and, in particular, in the range 200-250°C. However, it remains effective at temperatures exceeding 400°C as well.

5 For the purposes of the invention, the term "particles seeded with an oxidation catalyst" is intended to cover carbonaceous particles in and/or on which the soot oxidation catalyst SOC is dispersed in the form of very fine particles. Within the context of
10 the invention, the carbonaceous particles possess the feature of being already combined with the oxidation catalyst when they are placed in the presence of the nitrogen dioxide.

As far as the oxidation catalyst SOC is
15 concerned, it comprises at least one element selected from transition metals, alkali metals and alkaline earth metals, such as manganese, iron, copper, sodium, nickel and scandium, and the rare earth metals. These elements are preferably incorporated in the said
20 catalyst in the form of their oxides. The catalyst can of course comprise a plurality of elements, it being possible for each element to be present, independently of the others, in the form of its corresponding oxide or otherwise.

25 In accordance with a preferred embodiment of the invention, the oxidation catalyst is a compound containing at least one rare earth.

The expression "rare earth" is intended to denote the elements whose atomic number is between 57 and 71, and also yttrium.

Indeed, the rare earths, and especially the
 5 oxides of rare earths, such as, in particular, those of cerium, effectively catalyse the oxidation of carbonaceous materials.

As far as the rare earth is concerned, it can be selected more particularly from cerium, yttrium,
 10 neodymium, gadolinium, praseodymium, lanthanum and mixtures thereof. Cerium, lanthanum, neodymium, yttrium, praseodymium and mixtures thereof are particularly preferred. In the specific case of mixtures of rare earths, it is preferable for cerium
 15 and/or lanthanum to be predominant.

Within the scope of this invention it is also possible to use a compound containing at least one rare earth which comprises at least cerium in a mixture with one or more other elements.

20 As a representative of this other element, mention may be made more particularly of zirconium, alkali metals, alkaline earth metals and transition elements, such as the elements of groups IB, VIIA and VIII of the Periodic Table, especially copper,
 25 manganese and iron.

For the entirety of the specification, the Periodic Table is that published in the supplement to Bulletin de la Société Chimique de France, No. 1,

January 1996.

In their catalytic function, these metals are preferably in the form of their oxides.

The oxidation catalyst SOC, seeded at the
5 level of the soots, is advantageously incorporated into the latter via the introduction into the fuel of one of its derivatives such as a salt, sol or organic complex.

In the sense of the invention, the term "sol"
is intended to denote an organic colloidal suspension
10 based on at least one of the abovementioned elements.

Organic sols particularly suitable for the invention are those described in the applications EP 671 205, EP 737 236 and WO 97/19022. Regarding the preparation of these sols reference may also be made to
15 the teaching of these documents.

Another possibility consists in introducing the catalyst SOC in various forms, alternatively into the air at the intake of the engine or into the exhaust gas recirculation (EGR) circuit or at the exhaust
20 itself upstream of the particle filter.

Advantageously, the amount of oxidation catalyst SOC to be introduced into the engine is determined such that its content at the level of the carbonaceous particles reaches a level of between
25 approximately 0.1% and 30%, preferably between 0.1 and 15%, expressed by weight of the catalytic element relative to the weight of the soot. Advantageously, this content is at least 0.5% and, preferably, at least

2%.

As far as the nitrogen dioxide required for the combustion of the said carbonaceous particles is concerned, its concentration must be sufficient to enable the oxidation of the carbonaceous particles to be promoted.

As mentioned beforehand, the exhaust gases emitted by combustion engines may, in addition to the carbonaceous particles, comprise unburnt hydrocarbons, nitrogen monoxide, oxygen, carbon monoxide, carbon dioxide, nitrogen dioxide and possibly sulphur dioxide.

Naturally, nitrogen monoxide is present in a majority proportion relative to the nitrogen dioxide.

Consequently, the concentration of NO₂ at the exhaust must be sufficient to allow the oxidation of the carbonaceous particles, since a lack of NO₂ results in partial oxidation of the soots and hence in a progressive accumulation in the filter.

According to a first variant of the invention, it is possible to consider adjusting the concentration of nitrogen dioxide required for the combustion of the said carbonaceous particles by a change in engine control, performed continuously or discontinuously so as to induce the burning of the soots collected on the filter.

According to a second variant, which is the preferred variant to date, the amount of nitrogen dioxide required for the combustion of the carbonaceous

particles is generated catalytically. It is obtained by catalytic conversion of nitrogen monoxide.

Any known catalyst for converting nitrogen monoxide to nitrogen dioxide can be employed in the context of the present invention. In particular, it is possible to employ catalysts already used in the automotive sector for the catalytic conversion of exhaust gases.

By way of illustration of such catalysts, mention may be made in particular of those based on platinum, palladium, ruthenium, rhodium and their mixtures such as metal oxides of the platinum group, for instance rhodium oxide, Rh_2O_3 or the like. Also suitable are simple oxides or mixed oxides such as transition metal oxides and, more particularly, those based on cerium and/or manganese, such as CeO_2 , Mn_2O_3 , $Mn_2O_3-CeO_2$, $Mn_2O_3-CeO_2-ZrO_2$ and the perovskite systems.

These metals may be deposited on supports of the alumina, titanium, silica or zeolite type in a pure or doped form.

By way of illustration of this type of catalyst mention may be made more particularly of a catalyst based on platinum deposited on a lanthanum-doped titanium oxide. This type of catalyst is marketed by Rhodia (WO 97/49481).

The catalytic conversion of the nitrogen monoxide to nitrogen dioxide can be performed in accordance with two embodiments. It can be performed

either prior to the oxidation of the carbonaceous particles by the nitrogen dioxide thus formed, or concomitantly with the oxidation of the carbonaceous particles.

- 5 According to the first embodiment, the nitrogen monoxide is converted to nitrogen dioxide prior to the oxidation of the carbonaceous particles. Thus it is performed upstream of the filter containing the carbonaceous particles to be oxidized. To achieve
10 this, the exhaust gas containing nitrogen monoxide is contacted with a conversion catalyst, CC, situated upstream of the filter containing the carbonaceous particles to be oxidized. This conversion catalyst CC for converting nitrogen monoxide to nitrogen dioxide is
15 deposited on a support placed upstream of the filter containing the carbonaceous particles to be oxidized and through which the said exhaust gas passes before coming into contact with the filter comprising the said particles. In accordance with this embodiment, the
20 support and the filter are arranged in series.

- In such a case, it is desirable for the distance between them not to be too great, so as to prevent the incidence of thermodynamic equilibrium between the nitrogen monoxide and nitrogen dioxide,
25 which would tend to regenerate nitrogen monoxide. It is clear that this adjustment is within the expertise of the person skilled in the art.

 In a second embodiment of the invention, the

catalytic conversion of the nitrogen monoxide to nitrogen dioxide is carried out directly at the level of the filter on which the carbonaceous particles are collected. The catalyst required for the conversion of the nitrogen monoxide to nitrogen dioxide is therefore present, in this particular case, at the level of the filter containing the carbonaceous particles to be oxidized.

The catalyst for converting the nitrogen monoxide to nitrogen dioxide can be employed in the form of a layer applied to the surface of a support. This mode of application is more particularly preferred when the conversion is performed prior to the oxidation of the carbonaceous particles.

It is likewise possible to consider employing this conversion catalyst in a particulate form, especially in the form of granules, beads and cylinders. This second formulation is more particularly appropriate when the conversion of nitrogen monoxide to nitrogen dioxide and the oxidation of the carbonaceous particles by this nitrogen dioxide are performed concomitantly at the surface of the filter for carbonaceous particles to be oxidized.

A third embodiment of the invention consists in the catalyst for converting the nitrogen monoxide to nitrogen dioxide being combined with a so-called NO_x trap system. This is a catalyst system capable of oxidizing the nitrogen monoxide to nitrogen dioxide and

then adsorbing the nitrogen dioxide thus formed. The nitrogen dioxide stored in this way is released only under specific conditions. These specific conditions are linked, in particular, to the temperature and/or the oxygen/hydrocarbons ratio in the exhaust (N. Takahashi et al.; Catalysis Today; No. 27, 1996, 63-69). These No_x traps are generally based on platinum and barium.

According to one particular embodiment, this No_x trap system can consist of a composition comprising a support based on an oxide of cerium, an oxide of zirconium and an oxide of scandium or of a rare earth other than cerium and an active phase based on manganese and on at least one other element, selected from alkali metals, alkaline earth metals and rare earth metals. Also suitable is a composition comprising a supported phase containing manganese and at least one other element selected from terbium, gadolinium, europium, samarium, neodymium and praseodymium and a support based on cerium oxide or a mixture of cerium oxide and zirconium oxide.

These systems are generally provided in the form of powders and may if desired be shaped so as to be provided in the form of granules, beads, cylinders or honeycombs of varying dimensions. They may also be used in catalyst systems comprising a coating (washcoat) having catalytic properties and based on these systems, on a substrate of the metal monolith

type, for example, or made of ceramic.

An NO_x trap system of this kind can be employed in the context of the present invention in accordance with two embodiments.

5 According to a first embodiment, it is possible to consider depositing the system on the support comprising the conversion catalyst, CC, for converting the nitrogen monoxide to nitrogen dioxide, the said catalyst being placed upstream of the filter
10 containing the carbonaceous particles to be oxidized.

 According to a second embodiment, this NO_x trap system is deposited together with the conversion catalyst, CC, on the filter containing the carbonaceous particles to be oxidized.

15 According to one particular embodiment of the invention, the nitrogen dioxide is generated by passing the exhaust gases through a preferably monolithic support which is more preferably of the "ceramic honeycomb" type and on which is deposited at
20 least one catalyst for converting the nitrogen monoxide to nitrogen dioxide, preferably a platinum-based catalyst. The nitrogen dioxide generated in this way is subsequently transported by the exhaust gases to the filter comprising the carbonaceous particles to be
25 oxidized. The said filter is placed downstream of the support and at a distance sufficient for the nitrogen dioxide coming into contact with the particles to be present in an amount sufficient to ensure their

effective oxidation.

More particularly, as far as the filter on whose surface the carbonaceous particles are fixed is concerned, it can be conventional in form and

5 structure. Conventionally, it comprises one or more metal-mesh sieves through which the exhaust gases circulate. However, it may also be a filter of the "ceramic filtering wall" type or "ceramic foam" type, or may comprise fibre materials.

10 The process according to the invention makes it possible advantageously to carry out combustion at a range of temperatures which is significantly enlarged in comparison to the conventional processes. The results presented in the examples below specifically
15 illustrate this efficacy.

The examples and the figures presented hereinbelow are given by way of illustration and are not limitative of the present invention.

20 Figures:

Figure 1

Infrared analysis of the composition of control exhaust gas (with a catalyst for converting NO
25 to NO₂ and an alumina impregnated with 15% by weight of cerium) at the reactor outlet.

Figure 2

Infrared analysis of the composition of

control exhaust gases (with a catalyst for converting NO to NO₂ and unseeded soots) at the reactor outlet.

Figure 3

Infrared analysis of the composition of
5 exhaust gas seeded with a SOC catalyst and contacted with a catalyst CC, upstream of the reactor.

Figure 4

Infrared analysis of the composition of
seeded soots emerging from an engine and contacted with
10 a catalyst CC upstream of the reactor.

MATERIALS

In Examples 1 to 4 below, the conversion
15 catalyst, CC, employed at the inlet of the reactor is a conversion catalyst based on platinum deposited on a lanthanum-doped titanium oxide (WO 97/49481). This type of catalyst is very effective for oxidizing NO to NO₂ at 200°C and above.

20 In Examples 1 and 3, the alumina or soot employed at the reactor outlet is an industrial product. In these two examples, the alumina - CONDEA® marketed by CONDEA CHEMIE - or the soot (ref. ELFLEX 125 from CABOT) were impregnated beforehand with the
25 organic sol EOLYS® containing 25% by weight of Ce and marketed by Rhodia. Following impregnation, the product is dried at 100°C in air and then at 250°C in nitrogen

before being employed in the combustion test. The cerium oxide content was held constant at 15% by weight of the system.

In Example 4, the soot employed corresponds
5 to a soot collected (on an engine bench operating in accordance with the cycle UDC (European Urban Driving Cycle) in a particle filter. For this test, the gas-oil employed is admixed with 100 ppm of cerium from the organic sol EOLYS®.

10 The conditions of the test for oxidizing the NO and the soots employed for Examples 1 to 4 are identical and are described in Example 1.

The composition of the gases of the reactor outlet is analysed by FTIR, carried out directly
15 without condensing the effluents in order to avoid trapping of HNO_2 or HNO_3 , but with dilution of the stream of 30 l/h of reaction mixture with 90 l/h of dry nitrogen in order to escape the interfering effects of H_2O on the infrared analysis of NO and NO_2 . The FTIR
20 analyser used is that marketed by the NICOLET Company.

EXAMPLE 1

- In this Control Test 1 the system is composed
25 as follows:

- at the inlet, 50 mg of Pt/TiO_2 catalyst diluted in 150 mg of SiC ;
- at the outlet, 20 mg of Al_2O_3 impregnated with

15% CeO₂ diluted in 150 mg of SiC.

Following stabilization of the catalyst system at 150°C for 1 h subject to the stream of the reaction mixture - NO = 900 ppm, O₂ = 10%, H₂O = 10%,
5 made up to 100% with N₂ - the temperature of the reactor is taken from 150 to 400°C at 10°C/min and then stabilized at 400°C.

The results reported in Figure 1 show that:

From 220°C the Pt/TiO₂ catalyst is active in
10 the oxidation of NO to NO₂. The oxidation maximum of NO to NO₂ is of the order of 75% at 350°C and then stabilizes at 400°C and results in a ratio NO₂ = 65%/
NO = 35%.

No formation of CO is found, which confirms
15 that the alumina impregnated with 15% CeO₂ is inert to the reactions employed.

Consequently, this reference test shows that, in the absence of soot, the platinum-based catalyst oxidizes the NO to NO₂ from 220°C.

20

EXAMPLE 2

The procedure is as in Example 1, with the combination in this Control Test 2 of:

25 - at the reactor inlet: 50 mg of Pt/TiO₂ catalyst diluted in 150 mg of SiC;

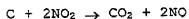
- at the reactor outlet: 20 mg of CABOT soot diluted in 150 mg of SiC.

The results reported on the graph in Figure 2 show that:

- 5 From 200°C, the Pt/TiO₂ catalyst oxidizes NO to NO₂ as in the control test of Example 1. The oxidation maximum is observed for a temperature of 350°C and then the concentration of NO₂ reduces very rapidly between 350 and 400°C. At the plateau temperature at
10 400°C no NO₂ is detected; all of the oxides of nitrogen are detected in the form of NO.

From 380°C, the CO content becomes significant, which indicates the beginning of slow combustion of the CABOT soot by the NO₂.

- 15 This second control test shows that, under the conditions of diesel application, the platinum-based catalyst oxidizes the NO to NO₂ from 200°C and then, from 350°C, the NO₂ formed on the catalyst is reduced by the carbon from the CABOT soot in accordance
20 with the chemical reactions



- which leads to equilibrium at 400°C at a level of NO which is identical to the original level and at a
25 concentration of NO₂ which is zero at the beginning of the plateau and then increases substantially over time.

EXAMPLE 3

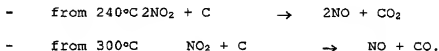
- The procedure is as in Example 1, with the
5 combination in Test 3 of:
- at the reactor inlet, 50 mg of the Pt/TiO₂
catalyst diluted in 150 mg of SiC;
 - at the reactor outlet, 20 mg of a CABOT soot
seeded with 15% by weight of CeO₂ from the additive
10 EOLYS® diluted in 150 mg of SiC.

The results reported in Figure 3 show that:

- the conversion of NO to NO₂ begins from 220°C;
around 240°C, an NO₂ content of the order of 10 ppm is
detected;
- 15 - from 240°C, NO₂ is no longer detected, which
is manifested in an NO signal which is identical to
that observed at the plateau of 150°C;
- from 300°C, significant formation of CO is
observed; the quantity of CO produced is of the order
20 of 100 ppm at 380°C;
- at the temperature of 400°C, analysis of the
reactor outlet gas reveals a CO content of zero and a
high level of oxidation of NO to NO₂.

This test of the invention shows that the
25 combination of a conversion catalyst and a soot seeded
with cerium oxide induces the combustion of the soot

from 240°C onwards. The reactions employed are as follows:



- 5 This manifests itself in an absence of NO₂ production between 240 and 400°C.

EXAMPLE 4

- 10 The procedure is as in Example 3, with the combination this time, in Test 4, of 50 mg of Pt/TiO₂ conversion catalyst and 20 mg of soot from an engine as a replacement for the CABOT soot described in Example 3.

- 15 Analysis of the chemical composition of this soot, collected in a particle filter mounted on a diesel vehicle operating with a gas-oil admixed with 100 ppm of the additive EOLYS marketed by Rhodia, shows that the CeO₂ content is 13.4% by weight relative to the
20 crude soot.

- The results reported in Figure 4 confirm the results of Test No. 4 which are characteristic of a commencement of oxidation of NO to NO₂ from 220°C onwards. Since all of the soot employed in the test is
25 oxidized by the NO₂ produced by the upstream catalyst, the outlet composition corresponds to an NO/NO₂ ratio which is characteristic of the activity of the Pt/TiO₂

catalyst.

The results obtained clearly show that:

- The inflammation temperature of the soots is lowered significantly when the carbon particles contain cerium oxide from an additive such as the product EOLYS®. In the absence of this additive, the reaction of oxidation of the carbon by the NO₂ produced on the platinum-based catalyst situated upstream takes place from 350°C as against 220°C when the soot contains cerium oxide.

- The concentration of NO₂ at the outlet of the reactor containing the combination at the inlet of an oxidation catalyst and at the outlet of an additivized soot is very strongly reduced up to 400°C. In the absence of cerium oxide dispersed in and/or on the soot and/or in the absence of soot downstream of the platinum-based oxidation catalyst, NO₂ is detected predominantly in the reaction stream. Under in-vehicle service conditions, this would be manifested in a discharge of nitric acid into the atmosphere.

CLAIMS

1. Process for the combustion treatment of carbonaceous particles collected on a filter situated in an exhaust circuit of an internal combustion engine, characterized in that the combustion of the said particles is brought about by contacting them with a gas mixture comprising at least nitrogen dioxide generated within the exhaust circuit of the said engine, the said particles having been seeded prior to their combustion with at least one catalyst of their oxidation.

2. Process according to claim 1, characterized in that the catalyst for oxidizing the said particles comprises at least one element selected from transition metals, alkali metals and alkaline earth metals, such as manganese, iron, copper, sodium, nickel and scandium, and the rare earth metals.

3. Process according to either of claims 1 and 2, characterized in that the catalyst for oxidizing the said particles is a compound containing at least one rare earth.

4. Process according to claim 3, characterized in that the rare earth is selected from cerium, yttrium, neodymium, gadolinium, praseodymium, lanthanum and mixtures thereof.

5. Process according to claim 3 or 4, characterized in that the compound containing at least one rare earth comprises cerium in a mixture with at least one other element selected from zirconium, alkali metals, alkaline earth metals and transition elements, such as the elements of groups IB, VIIA and VIII of the Periodic Table, especially copper, manganese and iron.

6. Process according to one of claims 2 to 5, characterized in that the element(s) are present in the catalyst independently of one another in the form of their respective oxide or otherwise.

7. Process according to one of claims 1 to 6, characterized in that the oxidation catalyst seeded at the level of the carbonaceous particles is incorporated therein via the introduction into the fuel of one of its derivatives such as a salt, sol or organic complex.

8. Process according to one of claims 1 to 6, characterized in that the oxidation catalyst is seeded at the level of the carbonaceous particles via its introduction alternatively into the air at the intake of the engine, or into the exhaust gas recirculation (EGR) circuit, or at the exhaust itself upstream of the particle filter.

9. Process according to one of claims 1 to 8, characterized in that the amount of oxidation catalyst seeded at the level of the carbonaceous particles is between 0.1% and 30%, preferably between 0.1% and 15%, expressed by weight of the catalytic element relative to the weight of the carbonaceous particle.

10. Process according to claim 9, characterized in that the amount of oxidation catalyst is at least 0.5% and, preferably, at least 2% expressed by weight of the catalytic element relative to the weight of the carbonaceous particle.

11. Process according to one of claims 1 to 10, characterized in that the concentration of nitrogen dioxide required for the combustion of the said carbonaceous particles is adjusted by a change in the control of the engine, performed continuously or discontinuously so as to induce the burning of the carbonaceous particles collected on the filter.

12. Process according to one of claims 1 to 10, characterized in that the concentration of nitrogen dioxide required for the combustion of the said carbonaceous particles is generated catalytically.

13. Process according to one of claims 1 to 10 and 12, characterized in that the nitrogen dioxide is generated by catalytic conversion of nitrogen monoxide.

14. Process according to claim 13, characterized in that the conversion of the nitrogen monoxide to nitrogen dioxide is performed in a step prior to the oxidation of the carbonaceous particles.

15. Process according to claim 14, characterized in that the conversion of the nitrogen monoxide to nitrogen dioxide is performed upstream of the filter containing the carbonaceous particles to be oxidized.

16. Process according to claim 14 or 15, characterized in that the conversion of the nitrogen monoxide to nitrogen dioxide is performed by contacting the exhaust gas with a

conversion catalyst, CC, for converting the nitrogen monoxide to nitrogen dioxide, which is present on a support which is situated upstream of the filter containing the carbonaceous particles to be oxidized and through which the said exhaust gas passes.

17. Process according to one of claims 1 to 10 and 12 and 13, characterized in that the conversion of the nitrogen monoxide to nitrogen dioxide is performed concomitantly with the oxidation of the carbonaceous particles by the nitrogen dioxide thus formed.

18. Process according to claim 17, characterized in that the catalytic conversion of the nitrogen monoxide to nitrogen dioxide is carried out at the level of the filter on which the carbonaceous particles to be oxidized are collected.

19. Process according to claim 18, characterized in that the catalyst permitting the conversion of the nitrogen monoxide to nitrogen dioxide is present at the level of the filter containing the carbonaceous particles to be oxidized.

20. Process according to one of claims 10 and 12 to 19, characterized in that the catalyst for converting the nitrogen monoxide to nitrogen dioxide is selected from those based on platinum, palladium, ruthenium, rhodium and their mixtures such as metal oxides of the platinum group, for instance rhodium oxide, Rh_2O_3 or the like as well as simple oxides or mixed oxides such as transition metal oxides such as those based on cerium and/or manganese, such as CeO_2 , Mn_2O_3 , $\text{Mn}_2\text{O}_3\text{-CeO}_2$, $\text{Mn}_2\text{O}_3\text{-CeO}_2\text{-ZrO}_2$ and the perovskite systems.

21. Process according to claim 20, characterized in that the catalyst is deposited on a support of the alumina, titanium, silica or zeolite type in a pure or doped form.

22. Process according to claim 21, characterized in that the catalyst for converting the nitrogen monoxide to nitrogen dioxide is based on platinum deposited on a lanthanum-doped titanium oxide.

23. Process according to one of claims 12 to 22, characterized in that the catalyst for converting the nitrogen monoxide to nitrogen dioxide is combined with a so-called NO_x trap system.

24. Process according to claim 23, characterized in that the system is a composition comprising a support based on an oxide of cerium, an oxide of zirconium and an

oxide of scandium or of a rare earth other than cerium and an active phase based on manganese and on at least one other element, selected from alkali metals, alkaline earth metals and rare earth metals or a composition comprising a supported phase containing manganese and at least one other element selected from terbium, gadolinium, europium, samarium, neodymium and praseodymium and a support based on cerium oxide or a mixture of cerium oxide and zirconium oxide.

25. Process according to one of claims 1 to 10 and 12 to 22, characterized in that the nitrogen dioxide is generated by passing the exhaust gases through a support on which is deposited at least one catalyst for converting the nitrogen monoxide to nitrogen dioxide so as to generate nitrogen dioxide which is subsequently transported by the exhaust gases to a metal filter comprising the carbonaceous particles to be oxidized, which filter is located downstream of the support and at a distance sufficient for the nitrogen dioxide coming into contact with the said carbonaceous particles to be present in an amount sufficient to ensure their effective oxidation.

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RHODIA CHIMIE

PROCESS FOR COMBUSTION TREATMENT OF CARBONACEOUS
PARTICLES IN AN EXHAUST CIRCUIT OF AN
INTERNAL COMBUSTION ENGINE

ABSTRACT

The invention relates to a process for the combustion treatment of carbonaceous particles collected on a filter situated in an exhaust circuit of an internal combustion engine, characterized in that the combustion of the said particles is brought about by contacting them with a gas mixture comprising at least nitrogen dioxide generated within the exhaust circuit of the said engine, the said particles having been seeded prior to their combustion with at least one catalyst of their oxidation.

No figure.

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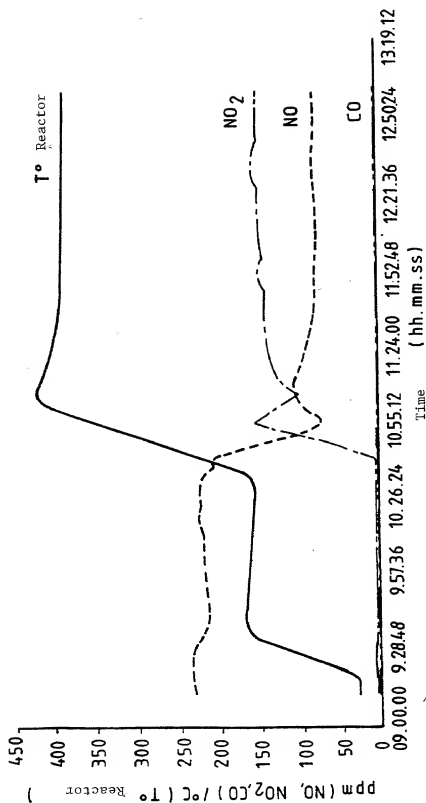


FIG.1

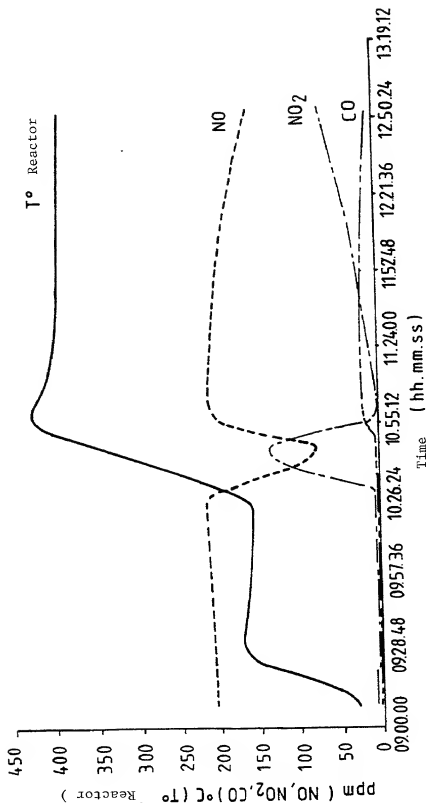


FIG. 2

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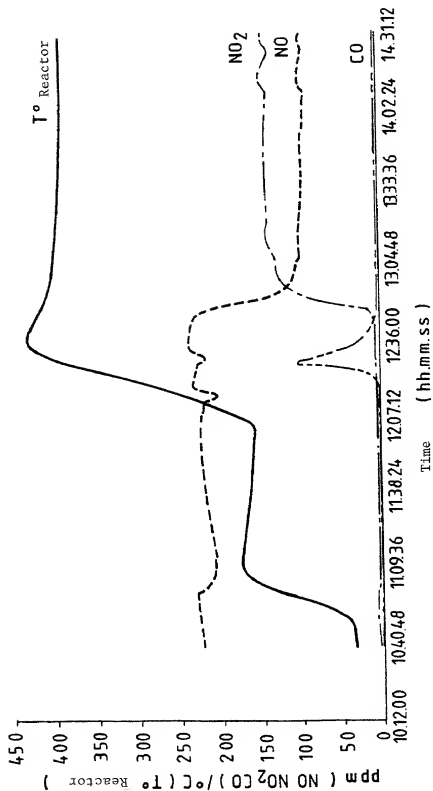
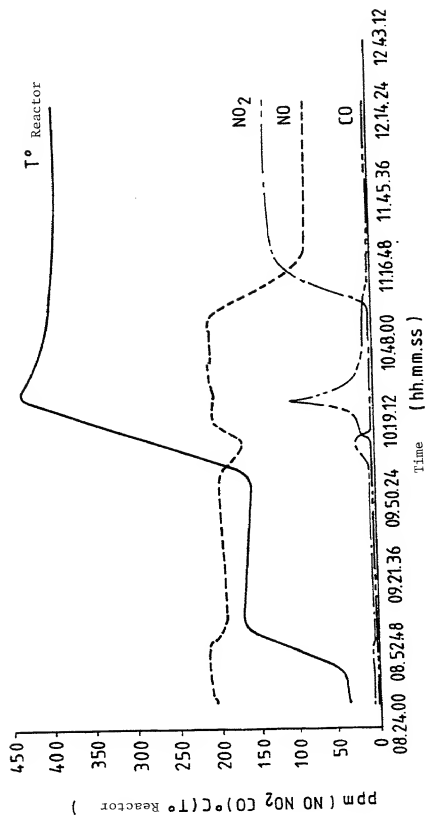


FIG. 3

FIG.4

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COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

022701-912

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;
I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

METHOD FOR TREATING BY COMBUSTION CARBON-CONTAINING PARTICLES IN AN

INTERNAL COMBUSTION ENGINE EXHAUST CIRCUIT

the specification of which (check only one item below):

☐ is attached hereto.

☐ was filed as United States application

Number _____

on _____

and was amended

on _____ (if applicable).

☒ was filed as PCT international application

Number PCT/FR99/01378

on 10 June 1999

and was amended

on _____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the Office all information known to me to be material to patentability as defined in Title 37, Code of Federal Regulations, §1.56.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 (a)-(e) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) of which priority is claimed:

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| COUNTRY (if PCT, indicate "PCT") | APPLICATION NUMBER | DATE OF FILING (day, month, year) | PRIORITY CLAIMED UNDER 35 U.S.C. §119 |
|-------------------------------------|--------------------|--------------------------------------|---|
| FR | 98/07859 | 22 June 1998 | <input checked="" type="checkbox"/> Yes <input type="checkbox"/> No |
| | | | <input type="checkbox"/> Yes <input type="checkbox"/> No |
| | | | <input type="checkbox"/> Yes <input type="checkbox"/> No |
| | | | <input type="checkbox"/> Yes <input type="checkbox"/> No |
| | | | <input type="checkbox"/> Yes <input type="checkbox"/> No |

I hereby claim the benefit under Title 35, United States Code § 119(e) of any United States provisional application(s) listed below.

(Application Number)

(Filing Date)

(Application Number)

(Filing Date)

COMBINED DECLARATION FOR PATENT APPLICATION AND POWER OF ATTORNEY (CONT'D)
(Includes Reference to Provisional and PCT International Applications)

Attorney's Docket No.

022701-912

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose to the Office all information known to me to be material to the patentability as defined in Title 37, Code of Federal Regulations §1.56, which became available between the filing date of the prior application(s) and the national or PCT international filing date of this application:

PRIOR U.S. APPLICATIONS OR PCT INTERNATIONAL APPLICATIONS DESIGNATING THE U.S. FOR BENEFIT UNDER 35 U.S.C. §120:

| U.S. APPLICATIONS | | STATUS (check one) | | |
|-------------------------|------------------|--------------------|---------|-----------|
| U.S. APPLICATION NUMBER | U.S. FILING DATE | PATENTED | PENDING | ABANDONED |
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PCT APPLICATIONS DESIGNATING THE U.S.

| PCT APPLICATION NO. | PCT FILING DATE | U.S. APPLICATION NUMBERS ASSIGNED (if any) | | |
|---------------------|-----------------|--|--|--|
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I hereby appoint the following attorneys and agent(s) to prosecute said application and to transact all business in the Patent and Trademark Office connected therewith and to file, prosecute and to transact all business in connection with international applications directed to said invention:

| | | | | | |
|---------------------------|--------|-------------------------|--------|------------------------|--------|
| William L. Mathis | 17,337 | Eric H. Weisblatt | 30,505 | Bruce T. Wieder | 33,815 |
| Robert S. Swecker | 19,885 | James W. Peterson | 26,057 | Todd R. Walters | 34,040 |
| Platon N. Mandros | 22,124 | Teresa Stanek Rea | 30,427 | Ronni S. Jilions | 31,979 |
| Benton S. Duffett, Jr. | 22,030 | Robert E. Krebs | 25,885 | Harold R. Brown III | 36,341 |
| Norman H. Stepno | 22,716 | William C. Rowland | 30,888 | Allen R. Baum | 36,086 |
| Ronald L. Grudziecki | 24,970 | T. Gene Dillahunty | 25,423 | Steven M. duBois | 35,023 |
| Frederick G. Michaud, Jr. | 26,003 | Patrick C. Keane | 32,858 | Brian P. O'Slaughnessy | 32,747 |
| Alan E. Kopsch | 25,813 | B. Jefferson Boggs, Jr. | 32,344 | Kenneth B. Leffer | 36,075 |
| Regis E. Slutter | 26,999 | William H. Benz | 25,952 | Fred W. Hathaway | 32,236 |
| Samuel C. Miller, III | 27,360 | Peter K. Skiff | 31,917 | Wendi L. Weinstein | 34,456 |
| Robert G. Mukai | 28,531 | Richard J. McGrath | 29,195 | Mary Ann Dillahunty | 34,576 |
| George A. Hovanec, Jr. | 28,223 | Matthew L. Schneider | 32,814 | | |
| James A. LaBarre | 28,632 | Michael G. Savage | 32,596 | | |
| E. Joseph Gess | 28,510 | Gerald F. Swiss | 30,113 | | |
| R. Danny Huntington | 27,903 | Charles F. Wieland III | 33,096 | | |



21839

and:

Address all correspondence to:



21839

Norman H. Stepno
BURNS, DOANE, SWECKER & MATHIS, L.L.P.
P.O. Box 1404
Alexandria, Virginia 22313-1404

Address all telephone calls to: Norman H. Stepno at (703) 836-6620.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

| | | | | | |
|--|--|--|--|---|--|
| FULL NAME OF SOLE OR FIRST INVENTOR <u>Gilbert BLANCHARD</u> | | SIGNATURE <u>X Gilbert Blanchard</u> | | DATE <u>X April 15th 2001</u> | |
| RESIDENCE <u>5, allée des Acacias, F-60330 Lagny le Sec, FR</u> <u>FR</u> | | | | CITIZENSHIP <u>FR</u> | |
| POST OFFICE ADDRESS | | | | | |
| <u>5, allée des Acacias, F-60330 Lagny le Sec, FR</u> | | | | | |
| FULL NAME OF SECOND JOINT INVENTOR, IF ANY <u>William MUSTEL</u> | | SIGNATURE <u>X William Mustel</u> | | DATE <u>X April 15th 2001</u> | |
| RESIDENCE <u>15, rue Feron, F-95160 Montmorency, FR</u> <u>FR X</u> | | | | CITIZENSHIP <u>FR</u> | |
| POST OFFICE ADDRESS | | | | | |
| <u>15, rue Feron, F-95160 Montmorency, FR</u> | | | | | |
| FULL NAME OF THIRD JOINT INVENTOR, IF ANY <u>Thierry SEGUELONG</u> | | SIGNATURE <u>X Thierry Segueulong</u> | | DATE <u>April 19th 2001</u> | |
| RESIDENCE <u>8, rue Rouget de Lisle, F-92800 Puteaux, FR</u> <u>FR X</u> | | | | CITIZENSHIP <u>FR</u> | |
| POST OFFICE ADDRESS | | | | | |
| <u>8, rue Rouget de Lisle, F-92800 Puteaux, FR</u> | | | | | |
| FULL NAME OF FOURTH JOINT INVENTOR, IF ANY | | SIGNATURE | | DATE | |
| RESIDENCE | | | | CITIZENSHIP | |
| POST OFFICE ADDRESS | | | | | |
| FULL NAME OF FIFTH JOINT INVENTOR, IF ANY | | SIGNATURE | | DATE | |
| RESIDENCE | | | | CITIZENSHIP | |
| POST OFFICE ADDRESS | | | | | |
| FULL NAME OF SIXTH JOINT INVENTOR, IF ANY | | SIGNATURE | | DATE | |
| RESIDENCE | | | | CITIZENSHIP | |
| POST OFFICE ADDRESS | | | | | |
| FULL NAME OF SEVENTH JOINT INVENTOR, IF ANY | | SIGNATURE | | DATE | |
| RESIDENCE | | | | CITIZENSHIP | |
| POST OFFICE ADDRESS | | | | | |
| FULL NAME OF EIGHTH JOINT INVENTOR, IF ANY | | SIGNATURE | | DATE | |
| RESIDENCE | | | | CITIZENSHIP | |
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